I
A NEW SYNTHESIS OF MANY-MEMBERED RINGS

II
RESTRICTED ROTATION ABOUT ALIPHATIC CARBON-CARBON BONDS

BY

LYNWOOD NELSON WHITEHILL

A.B., Dartmouth College, 1935

M.A., Dartmouth College, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1941

URBANA, ILLINOIS

1941

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549818_0114

I
A NEW SYNTHESIS OF MANY-MEMBERED RINGS

II
RESTRICTED ROTATION ABOUT ALIPHATIC CARBON-CARBON BONDS

BY

LYNWOOD NELSON WHITEHILL

A.B., Dartmouth College, 1935

M.A., Dartmouth College, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1941

URBANA, ILLINOIS

1941

ACKNOWLEDGMENT

The author wishes to express his gratitude and appreciation to Professor Roger Adams for suggesting these problems and for his cooperation and valuable suggestions during the course of the investigations.

I. A NEW SYNTHESIS OF MANY-MEMBERED RINGS

INTRODUCTION

Two general methods have been used for the synthesis of compounds containing many-membered rings. The high dilution technique[1] has been employed successfully by allowing appropriate bifunctional molecules to react in solutions so dilute that intramolecular reaction predominated over possible intermolecular condensations. Carothers[2] has obtained cyclic anhydrides and lactones by depolymerization of linear polymers.

The present research has been concerned with the possibility of obtaining many-membered rings by allowing two bifunctional molecules to react with each other at high dilution. More particularly, a study of the synthesis of cyclic ethers from ω, ω'-dibromides and hydroquinone has been made.

EXPERIMENTAL AND DISCUSSION

In this work 1, 1′, 4, 4′-*bis*-(trimethylenedioxy)-dibenzene was synthesized in the following way: hydroquinone→hydroquinone-*bis*-(3-bromopropyl) ether → 1, 1′, 4, 4′-*bis*-(trimethylenedioxy)-dibenzene. The last step was carried out at high dilution using equimolecular amounts of hydroquinone and hydroquinone-*bis*-(3-bromopropyl) ether. This method gave a better yield than the intramolecular ring closure: hydroquinone-*bis*-(3-bromopropyl) ether → α-*p*-hydroxyphenoxy-γ-(*p*-γ-bromopropoxyphenoxy)-propane → 1, 1′, 4, 4′-*bis*-(trimethylenedioxy)-dibenzene.

By the former method 1, 1′, 4, 4′-*bis*-(hexamethylenedioxy)-dibenzene was also synthesized. Attempts to prepare 1, 1′, 4, 4′-*bis*-(ethylenedioxy)-dibenzene in this way were unsuccessful.

II. RESTRICTED ROTATION ABOUT ALIPHATIC CARBON-CARBON BONDS

INTRODUCTION

Considerable physico-chemical evidence has been produced from dipole moment data to indicate that restricted rotation about aliphatic carbon-carbon single bonds is possible. This phenomenon has not been demonstrated by the chemical method of resolution.

The present research has been concerned with an attempt to synthesize molecules which on the basis of models developed by Stuart[3] might exhibit this type of restricted rotation.

EXPERIMENTAL AND DISCUSSION

The molecule chosen for synthesis was 2-methyl-3-chloro-4-*o*-tolyldiphenyl-2-butenoic acid. The proposed method of synthesis required the preparation of *o*-tolyldiphenylmethyl-ethyl ketone. The two methods used in an attempted synthesis of this ketone were: (I) benzoin → *o*-tolylhydrobenzoin → *o*-tolyldiphenylacetaldehyde → *o*-tolyldiphenylmethyl-ethyl carbinol → *o*-tolyldiphenylmethyl-ethyl ketone and (II) *o*-tolyldiphenylmethylcarbinol → *o*-tolyldiphenylchloromethane → *o*-tolyldiphenylacetic acid → *o*-tolyldiphenylacetyl chloride → *o*-tolydiphenylmethyl-ethyl ketone. The first method failed in the third step since addition of ethylmagnesium iodide to the aldehyde could not be effected even though methylmagnesium iodide gave an 88 per cent yield of addition product under the same conditions. The second method was successful. The proposed preparation of the desired acid from this ketone is as follows: ketone→ β-keto-α-methyl-γ-*o*-tolyldiphenylbutyric acid → 2-methyl-3-chloro-4-*o*-tolyldiphenyl-2-butenoic acid. Treatment of the ketone with excess ethylmagnesium iodide according to the method of Fuson, Fugate, and Fisher[4] should give the β-ketonic acid readily since this reaction goes smoothly when *o*-tolyldiphenylmethyl-methyl ketone is used. The last step has not been worked out.

BIBLIOGRAPHY

[1] Lüttringhaus and Ziegler, Ann., **528**, 155 (1937).

[2] Carothers and Hill, J. Am. Chem. Soc., **55**, 5023, 5031 (1933).

[3] Stuart, Z. physik. Chem., **B27**, 350 (1934).

[4] Fuson, Fugate, and Fisher, J. Am. Chem. Soc., **61**, 2362 (1939).

VITA

The writer was born in Groton, Vermont, on May 10, 1913. He received his elementary education in the public schools of Groton and Passumpsic, Vermont, and was graduated from St. Johnsbury Academy in St. Johnsbury, Vermont, in June, 1931. In September, 1931, he entered Dartmouth College from which he was graduated in 1935. During the years 1935-1937 he was an instructor of chemistry at Dartmouth College and received the degree of Master of Arts from this school in 1937. He entered the University of Illinois in 1937 where he held a Cramer Foundation Fellowship during 1937-1938 and a teaching assistantship from 1938 to 1941.